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AN INDICATOR STUDY OF ACETIC ACID - ACETIC ANHYDRIDE MIXTURES USING THYMOL BLUE AND A RE-INTERPRETATION OF THE KINETICS OF THE ACETYLATION OF SULPHURIC ACID

by

H. A. E. MACKENZIE

OPSOMMING

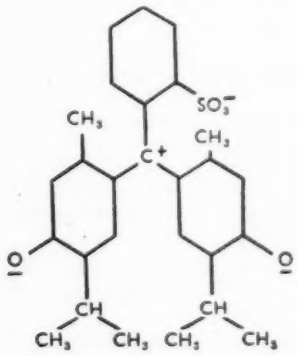
Die gedrag van timol-blou as indikator in mengsels van asynsuur en asynsuuranhidried is spektrofotometries bestudeer. Die resultate is in terme van 'n „asetiel-ioon-funksie" van die oplosmiddel weergegee en is gebruik om die asetilering van swawelsuur in mengsels van asynsuur en asynsuuranhidried kwantitatief te verklaar. 'n Kwalitatiewe verklaring word gegee vir die feit dat die elektrolitiese geleidingsvermoë van swawelsuur in asynsuur verhoog word deur die byvoeging van asynsuuranhidried.

SUMMARY

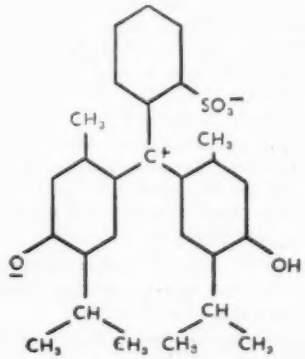
The indicator behaviour of thymol blue in acetic acid-acetic anhydride mixtures has been studied spectrophotometrically. The results have been interpreted in terms of an "acetyl ion function" of the medium and used to provide a quantitative explanation of the acetylation of sulphuric acid in acetic acid-acetic anhydride mixtures. The fact that the electrolytic conductance of sulphuric acid in acetic acid is enhanced by the addition of acetic anhydride is explained qualitatively.

Indicator behaviour of thymol blue in aqueous solution

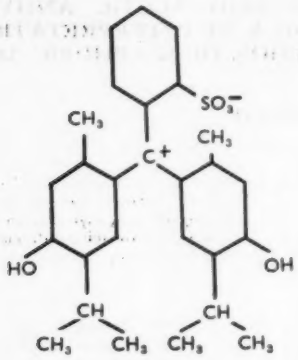
The colour changes of thymol blue which are effected by alterations in the acidity of an aqueous medium in which it is dissolved are now fairly well understood. The alkaline form of the indicator is a doubly charged anion[1] (**I**). This is blue-violet in colour due to an absorption band with $\lambda_{max} = 595$ mμ[2, 3]. With increasing acidity of the medium, (**I**) is converted by a simple proton transfer to the singly charged anion (**II**), which is yellow in colour and has $\lambda_{max} = 460$ mμ[3]. (**II**) is in turn converted into the neutral molecule (**III**) by a further increase in acidity. In form (**III**) the indicator is magenta in colour and its extinction curve shows an absorption band with $\lambda_{max} =$ 544 mμ[2, 3, 4]. In agreement with this formulation are the facts that, in dilute aqueous solution, the monosodium salt of the indicator is yellow, whereas the disodium salt is blue[5]. Kolthoff[6] has suggested that the cation (**IV**) may be formed from (**III**), producing evidence in favour of this suggestion from studies in adsorption of the indicator on negatively charged precipitates.



I.



II.



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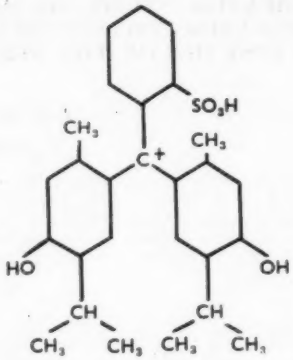


IV.

The equilibrium, (I) + $H^+ \rightleftarrows$ (II), will not concern us in the present studies. For the reaction (II) + $H^+ \rightleftarrows$ (III), the equilibrium constant is given[4, 7] by pK = 1·62± 0·02; the other values which have been obtained[2, 3] have been critically discussed by Kolthoff[7], and are probably inaccurate.

Indicator behaviour of thymol blue in acetic acid-acetic anhydride mixtures

In Fig. 1 are given the extinction curves for solutions of thymol blue in acetic acid, in 95 per cent v/v acetic anhydride and in various other acidic media. The thymol blue was Merck's "Thymolblau zur Bestimmung der Wasserstoff-Ionen Konzentration". Acetic acid and acetic anhydride were purified in the manner previously described[8]. All the indicator solutions contained about 20 mg. of the solid per litre. Density measurements were made with a Beckmann Model DU Quartz spectrophotometer using 1·002 cm. cells and in all cases the solvent was used as a comparison liquid.

An inspection of the curves reveals several points of interest. The indicator is completely in its acid form in 5N and 10N aqueous hydrochloric acid solutions, since the extinction curves for these two media coincide. The form (III) is characterized by two absorption bands with $\lambda_{max} = 550$ mμ and $\lambda_{max} = 390$ mμ. The latter does not seem to have been reported previously. If solid thymol blue is assumed to be the monohydrate[5] and therefore of molecular weight 484·6, the molar extinction coefficients are spectively $\epsilon_{max} = 2{\cdot}59 \times 10^4$ and $\epsilon_{max} = 7{\cdot}81 \times 10^3$. The isosbestic[9] point for aqueous solutions of the indicator is at $\lambda = 485$ mμ in agreement with Brode's figure[3]. In weakly acid solutions of the indicator the absorption band for (II) becomes evident at $\lambda_{max} = 430$ mμ, a value somewhat different from that reported by Holmes and Snyder[3]. The proximity of this band, it may be noted, to the secondary maximum of form (III) may lead to confusion in studies with mixed solvents where shifts in the values of λ_{max} are likely to occur.

In pure acetic acid the indicator appears to be completely in form (III) but the positions of the two maxima are somewhat different: viz. at 548 mμ, $\epsilon_{max} = 2{\cdot}47 \times 10^4$ and at 394 mμ, $\epsilon_{max} = 6{\cdot}99 \times 10^3$.

The applicability of Beer's law to light absorption by the indicator in acetic acid has been verified and the results are given in Table I. The solutions were prepared by successive volumetric dilutions of a more concentrated solution.

FIGURE 1

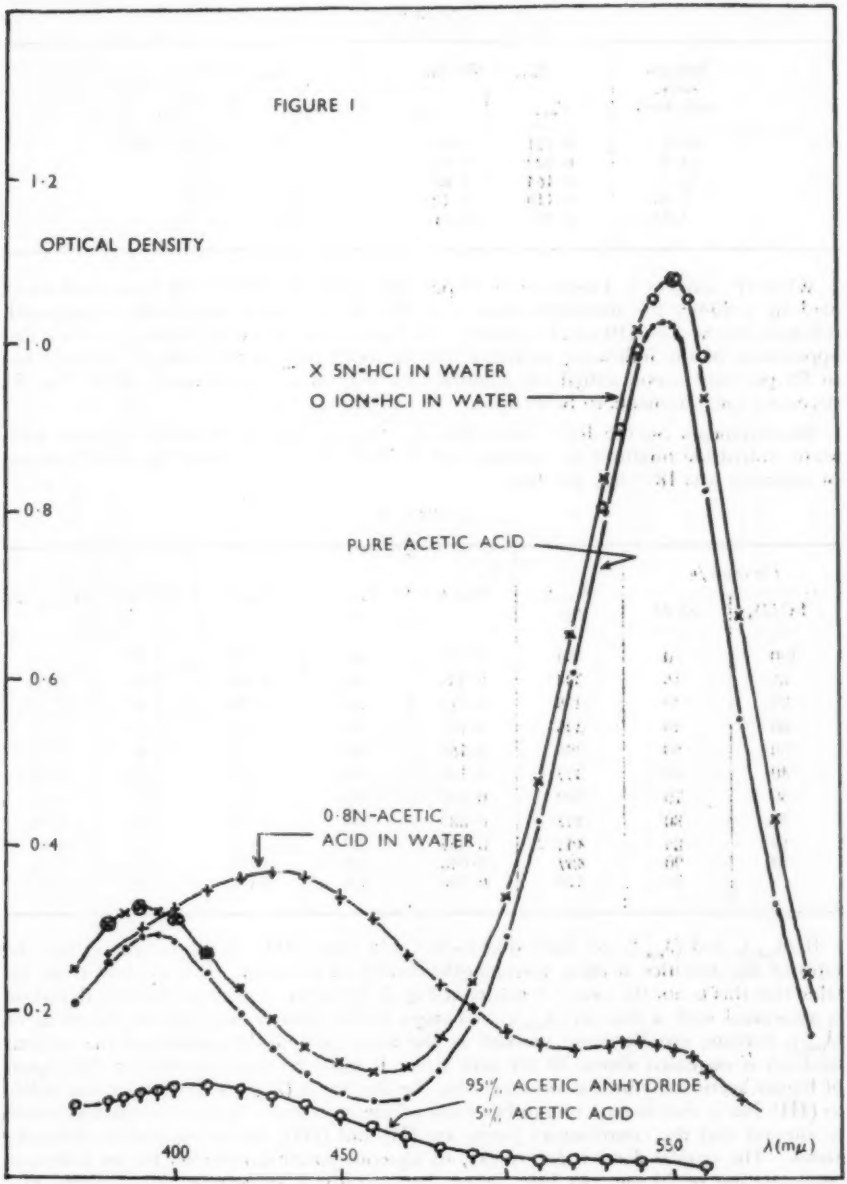

1·2
OPTICAL DENSITY
1·0
X 5N-HCl IN WATER
O ION-HCl IN WATER
0·8
PURE ACETIC ACID
0·6
0·8N-ACETIC
ACID IN WATER
0·4
0·2
95% ACETIC ANHYDRIDE
5% ACETIC ACID
400
450
550
λ(mμ)

TABLE I

Indicator concn. (mg./litre)	$\lambda_{max} = 394\ m\mu$.		$\lambda_{max} = 548\ m\mu$.	
	d_{max}	ϵ_{max}	d_{max}	ϵ_{max}
18·7	0·271	$7{\cdot}01 \times 10^3$	0·955	$2{\cdot}47 \times 10^4$
14·9	0·222	7·20	0·782	2·53
11·2	0·164	7·08	0·582	2·51
7·46	0·110	7·12	0·383	2·48
3·74	0·059	(7·6)	0·203	(2·6)

When the solvent is a mixture of 95 per cent acetic anhydride and 5 per cent acetic acid by volume, the maximum near $\lambda = 550$ mμ is almost completely suppressed, whereas one at $\lambda = 410$ mμ is evident. In pure acetic anhydride there is a slow disappearance of the indicator, probably due to acetylation of the hydroxy groups, but in 95 per cent acetic anhydride solutions the indicator is sufficiently stable for the necessary measurements to be effected.

Measurements on the light absorption by thymol blue in a series of acetic acid-acetic anhydride mixtures are summarized in Table II. In all cases the concentration of indicator was 18·7 mg. per litre.

TABLE II

Per cent v/v		$(\lambda_{max})_1$	$(d_{max})_1$	$(\lambda_{max})_2$	$(d_{max})_2$	$\log(d_1/d_2)$	$\log(c_V/c_{III})$
$(AcOH)_2$	Ac_2O	mμ		mμ			
100	0	394	0·271	548	0·955	$\bar{1}$·45	—
85	15	394	0·239	548	0·856	$\bar{1}$·45	$\bar{1}$·06
70	30	395	0·212	546	0·746	$\bar{1}$·45	$\bar{1}$·45
60	40	395	0·187	545	0·637	$\bar{1}$·47	$\bar{1}$·70
50	50	396	0·168	544	0·538	$\bar{1}$·47	$\bar{1}$·89
40	60	397	0·136	544	0·402	$\bar{1}$·53	0·14
30	70	399	0·099	543	0·265	$\bar{1}$·57	0·41
20	80	402	0·082	541	0·143	$\bar{1}$·80	0·76
15	85	403	0·087	540	0·092	$\bar{1}$·98	0·97
10	90	407	0·096	540	0·047	0·31	1·28
5	95	410	0·108	536	0·022	0·69	2·6

If $(\lambda_{max})_1$ and $(\lambda_{max})_2$ are both due to the acid form (III) of the indicator then the ratio of the densities at these wavelengths should be constant. It is evident from the table that this is not the case. A glance at Fig. 2, however, will show that this deviation is associated with a shift in $(\lambda_{max})_1$. Changes in the density ratio and in the value of $(\lambda_{max})_1$ become rapidly more marked as the acetic anhydride content of the solvent medium is increased above 70 per cent v/v. It must be assumed that, in the region of higher acetic anhydride concentrations, the density at $(\lambda_{max})_1$ is no longer due solely to (III), but is due in part to another form of the indicator. It might seem reasonable to suggest that the contributory forms are (II) and (III), but an immediate difficulty arises. The optical density due to (II) in aqueous solution is 0·365 for an indicator concentration of 20 mg. per litre, when the indicator is *by no means* all in form (II);

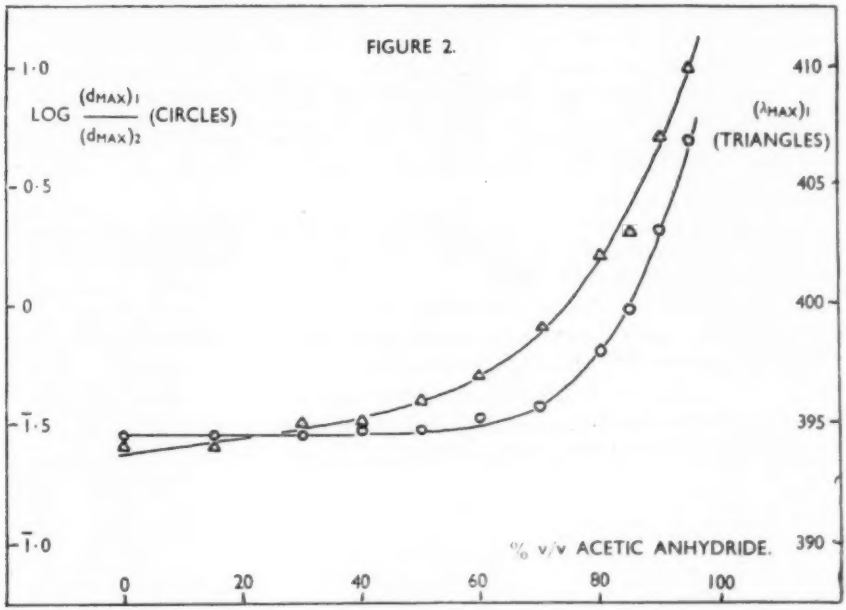


FIGURE 2.
LOG (dMAX)1 / (dMAX)2 (CIRCLES)
(λMAX)1 (TRIANGLES)
1·0
0·5
0
1̄·5
1̄·0
410
405
400
395
390
% v/v ACETIC ANHYDRIDE.
0
20
40
60
80
100

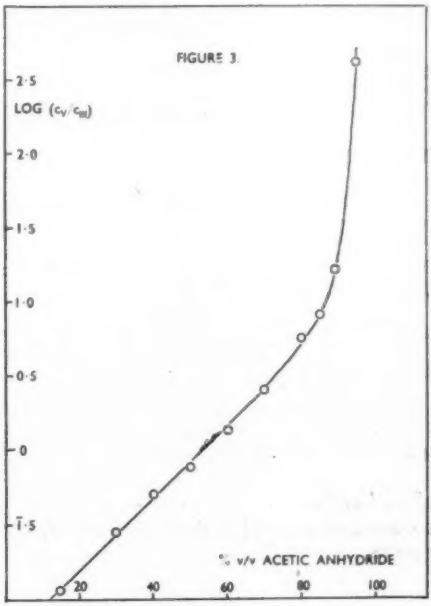


FIGURE 3.
LOG (cv/cm)
2·5
2·0
1·5
1·0
0·5
0
1̄·5
% v/v ACETIC ANHYDRIDE
20
40
60
80
100

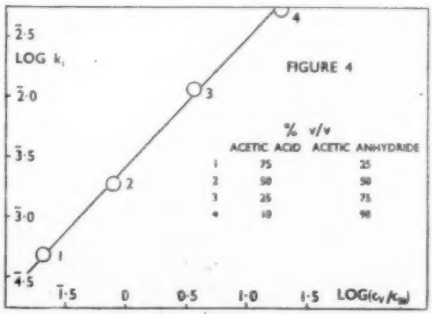


FIGURE 4
LOG k1
2̄·5
2̄·0
3̄·5
3̄·0
4̄·5
1̄·5
0
0·5
1·0
1·5
LOG(cv/cm)
% v/v
ACETIC ACID
ACETIC ANHYDRIDE
1 75 25
2 50 50
3 25 75
4 10 90

yet $(d_{max})_1$ in 95 per cent acetic anhydride is only 0·108 for the same indicator concentration, when the indicator exists as (**III**) to a negligible extent. (See Fig. 1).

It is hardly probable, therefore, that $(d_{max})_1$ in acetic anhydride is due to (**II**), since this would imply a threefold change at least in the molar extinction coefficient for a change in medium from water to acetic anhydride. The conclusion is that the light absorption at $(\lambda_{max})_1$, for mixtures of acetic acid and acetic anhydride, is due to (**III**) and some other form of the indicator not yet considered.

Interpretation of results

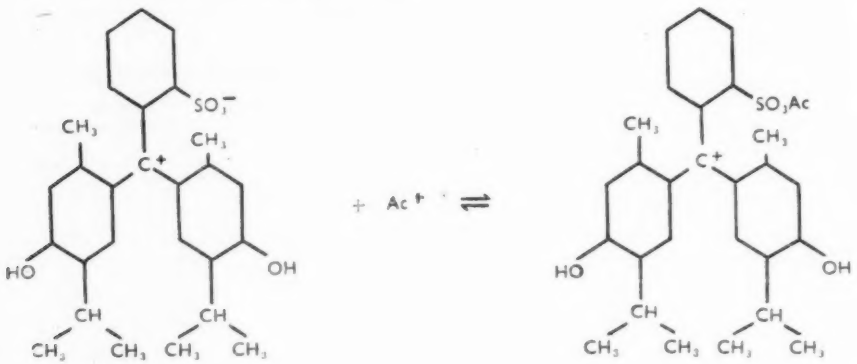
Mackenzie and Winter[10] have suggested that in acetic acid-acetic anhydride solutions of mineral acid the strongly electrophilic solvated proton, $AcOH_2^+$, reacts with acetic anhydride according to the equation

$$AcOH_2^+ + Ac_2O \rightleftharpoons Ac^+ + (AcOH)_2.$$

Presumably the acetyl ion will exist even in simple mixtures of acetic acid and acetic anhydride since the $AcOH_2^+$ ion is produced by the autoprotolysis reaction

$$(AcOH)_2 \rightleftharpoons AcOH_2^+ + AcO^-.$$

By analogy with Kolthoff's suggestion that (**IV**) may be formed in highly acid solutions, the following reaction is now proposed:



III. V.

The thermodynamic equilibrium constant for the reaction is given by

$$K = (a_{Ac}{}^+ . a_{III})/a_V, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{or} \quad pK = -\log(a_{Ac}{}^+ . f_{III}/f_V) + \log(c_V/c_{III}), \quad \ldots\ldots\ldots\ldots\ldots (2)$$

where the a are activities and the f are activity coefficients. Following Braude's[11] modified definition of the acidity function introduced by Hammett[12], we may define a quantity, $H_{Ac}{}^+$, which we shall call the *acetyl ion function*, and which measures the tendency of a medium to transfer an acetyl ion to a neutral base dissolved therein, by the equation

$$H_{Ac}{}^+ = \log(a_{Ac}{}^+ . f_B/f_{BAc}{}^+). \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

In the case of thymol blue the base and its conjugate acetyl ion derivative are (III) and (V) respectively so that equation (3) becomes

$$H_{Ac}^{+} = \log(a_{Ac}^{+} . f_{III}/f_V). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

From (2) and (4) it follows that

$$H_{Ac}^{+} = -pK + \log(c_V/c_{III}). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

The acetyl ion function of the solution is thus proportional to the logarithm of the indicator ratio, c_V/c_{III}. Values of this ratio for thymol blue in acetic acid-acetic anhydride mixtures are given in Table II and plotted in Fig. 3. c_V is obtained by difference from the known total concentration of indicator and the measured concentration of **(III)**.

The acetylation of sulphuric acid in acetic acid-acetic anhydride mixtures

Murray and Kenyon[13] have studied the acetylation of sulphuric acid, but have obtained no very convincing explanation of the variation of the specific reaction rate with the composition of the reaction mixture. If it is remembered that sulphuric acid is but feebly ionized in acetic acid[10] and therefore exists chiefly in the molecular form H_2SO_4, then the following equilibrium may be proposed:—

$$(HO)_2SO_2 + Ac^{+} \rightleftarrows (HO)_2SO_2 . Ac^{+}.$$

It will be noticed that this is essentially similar to the indicator equilibrium

$$\textbf{(III)} + Ac^{+} \rightleftarrows \textbf{(V)}$$

proposed earlier. If the rate determining process in the acetylation of sulphuric acid is taken to be the first order decomposition

$$(HO)_2SO_2 . Ac^{+} \longrightarrow \begin{matrix} HO{-}SO_2 \\ | \\ CH_2 . COOH \end{matrix} + H^{+},$$

then the rate of the reaction, v, is given by

$$v = k . c_{H_2SO_4 \cdot Ac^{+}},$$

and, since the thermodynamic equilibrium constant for the acetyl ion addition to sulphuric acid is

$$K = a_{H_2SO_4 \cdot Ac^{+}}/a_{Ac^{+}} . a_{H_2SO_4},$$

we have $$v = kK . (a_{Ac^{+}} . f_{H_2SO_4}/f_{H_2SO_4Ac^{+}}) . c_{H_2SO_4}.$$

The first order specific reaction rate for the disappearance of sulphuric acid is thus

$$k_1 = kK . (a_{Ac^{+}} . f_{H_2SO_4}/f_{H_2SO_4Ac^{+}})$$

and $$\log k_1 = \log\left(\frac{kK . f_{(H_2SO_4)}}{f_{(H_2SO_4Ac^{+})}} . \frac{f_{BAc^{+}}}{f_B}\right) + \log(a_{Ac^{+}} . f_B/f_{BAc^{+}}).$$

By the definition of H_{Ac}^{+} (equation 3) it follows that

$$\log k_1 = \log(kK . X) + H_{Ac^{+}},$$

where X represents the activity coefficient ratio in the preceding equation. It may be argued, on the lines adopted by Hammett[12], that X will not be significantly affected by changes in medium composition, so that the plot of $\log k_1$ against the acetyl ion function should be linear and of unit slope. Because of the relation (5), the plot of $\log k_1$ against $\log(c_V/c_{III})$ should also be linear and of unit slope. This plot is given in Fig. 4. The values of k_1 are those of Murray and Kenyon (*loc. cit.*) and the values of (c_V/c_{III}) are those obtained in this work. Over the range of solvent mixtures from 20 per cent v/v to 90 per cent v/v acetic anhydride the plot is linear. The slope is not quite unity, but when it is borne in mind that the rate constants were determined at 40°C., whereas the indicator ratios were measured at room temperature, the agreement is sufficiently good to be convincing.

The conductance of sulphuric acid in acetic acid-acetic anhydride mixtures

The interesting point that sulphuric acid is basic with respect to acetic anhydride emerges from the above treatment. This concept provides an immediate explanation of the observation made by Kolthoff and Willman[14] that the conductance of sulphuric acid in acetic acid is enhanced by the addition of acetic anhydride. In pure acetic acid the conductance of sulphuric acid is so low that it must be regarded as a weak electrolyte. The addition of acetic anhydride, however, in the light of the above concepts, may be expected to bring about the reaction

$$(HO)_2SO_2 + Ac_2O \rightleftarrows (HO)_2SO_2.Ac^+ + OAc^-,$$

thus giving rise to a greater conductance.

The author wishes to thank Professor F. L. Warren for placing at his disposal the Beckmann spectrophotometer used for the indicator studies.

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REFERENCES

[1] Kolthoff and Guss, *J. Amer. Chem. Soc.*, 1938, **60**, 2516; Schwarzenbach, *Helv. Chim. Acta.*, 1937, **20**, 490.
[2] Brode, *J. Amer. Chem. Soc.*, 1924, **46**, 581.
[3] Holmes and Snyder, *ibid.*, 1925, **47**, 224.
[4] Masi and Knight, *ibid.*, 1945, **67**, 1558.
[5] Orndorff and Cornwell, *ibid.*, 1926, **48**, 981.
[6] Kolthoff, *J. Phys. Chem.*, 1931, **35**, 1442.
[7] *idem., ibid.*, 1930, **34**, 1475.
[8] England and Mackenzie, This Journal. 1949, **2**, 145.
[9] Brode, "Chemical Spectroscopy", 2nd Ed., John Wiley & Sons, 1943, 250.
[10] Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159.
[11] Braude and Stern, *J. Chem. Soc.*, 1948, 1971.
[12] Hammett, "Physical Organic Chemistry", McGraw-Hill, 1940, 267.
[13] Murray and Kenyon, *J. Amer. Chem. Soc.*, 1940, **62**, 1230.
[14] Kolthoff and Willman, *ibid.*, 1934, **56**, 1007; see also the discussion in reference [10].

THE SAPONINS

PART I. THE ISOLATION OF GITOGENIN AND DIGITOGENIN FROM *CESTRUM LÆVIGATUM*

by

P. A. S. CANHAM and F. L. WARREN

OPSOMMING

Daar word aangetoon dat die groen bessies van *Cestrum lævigatum*, die bossie wat „Chase Valley"-siekte veroorsaak, saponiene bevat. Hidrolise van die gemengde saponiene lewer die sapogeniene op wat as die asetate afgeskei en as gitogenien en digitogenien geïdentifiseer word.

SUMMARY

The green berries of *Cestrum lævigatum*, the plant responsible for the "Chase Valley" disease of cattle, are shown to contain saponins. Hydrolysis of the mixed saponins gave the sapogenins which were separated as their acetates and identified as gitogenin and digitogenin.

"Chase Valley" disease of cattle has been the cause of stock losses in Natal in the dry winter months (May, June and July) for over forty years. With the botanical assistance of Professor A. W. Bayer, Thorburn[1] traced the disease to *Cestrum lævigatum* Schlecht (Inkberry plant).

Preliminary experiments on the alcoholic extracts of the plant indicated the presence of saponins, but a solid saponin could not be isolated. The small green berries which appeared during May and June produced very pronounced foaming on shaking with water, and alcoholic extraction gave about two per cent of a solid glycosidal mixture which could not be separated into pure components.

Hydrolysis of the mixed glycosides gave reducing sugars and a solid having a melting point 283°, which remained constant under different conditions of crystallization, and was thought to be a new sapogenin. Acetylation, however, gave a mixture of acetates which was readily separated into the less soluble gitogenin diacetate and the more soluble digitogenin triacetate. The two acetates were readily hydrolysed to gitogenin and digitogenin. The melting points of digitogenin and its acetate showed no depression on admixture with authentic specimens obtained from digitonin. It is of interest, however, that digitogenin when mixed with small quantities of gitogenin showed a melting point of 283°.

	Found	*Recorded m.p.*
Gitogenin $C_{27}H_{44}O_4$	268 – 270°	272°, 268°[2]
Gitogenin diacetate $C_{31}H_{48}O_6$ ..	242°	242°, 243°, 244°[2, 3]
Digitogenin $C_{27}H_{44}O_5$	284 – 285°	284°[5]
Digitogenin triacetate $C_{33}H_{50}O_8$ ..	190°	190°[5]

Since drastic hydrolysis of the steroidal saponins sometimes causes structural changes[4], the enzymatic hydrolysis of the mixed saponins was also effected by a method used successfully by Jacobs and Hoffmann for the hydrolysis of cymarin[6]. An enzyme, cestrinase, was first isolated from the defatted, dried, green berries and allowed to react with the mixed saponins in a solution buffered to pH 5·6. Under these conditions it was possible to isolate gitogenin free from digitogenin. It is of interest that after isolation, the glycosides exhibited little solubility in alcohol with which they were originally extracted. Furthermore, whereas the extract foamed copiously, the dried mixed glycosides did not readily show this characteristic. This phenomenon might be explained by some partial hydrolysis and the formation of digitonides.

To obtain further information on the toxicity of the plants, semi-quantitative extractions were carried out on the different portions. The leaves, flowers and ripe black berries contained only small traces of saponin compared with the small green berries;

thus chemical confirmation is afforded of the observation that the plant is most toxic during the winter months and this high toxicity may be attributed to the unripe berries.

Experiments carried out with the isolated saponins at the Allerton Veterinary Laboratories by the kindness of the Director, showed post-mortem lesions characteristic of the "Chase Valley" disease which may thus be attributed to the hæmolytic action of gitonin and digitonin.

In view of the difficulties attending the collection of these minute berries and the small quantity available, it was not possible to separate the saponins as such. This will be studied further with a view to investigating the sugar moiety when it is again possible to collect samples.

EXPERIMENTAL

Extraction of saponins

(i) Fresh green berries (100 g.) were treated with ether vapour and subjected to infra-red rays (temperature 42°) for three hours when complete desiccation was effected. The dried berries were ground to a fine powder (60 g.) and extracted with ether in a Soxhlet extraction apparatus. The ether extract contained no aglycone. The resulting defatted and chlorophyll-free berries (50 g.) were extracted five times with boiling 95 per cent ethanol (5 × 250 ml.), the extract concentrated under reduced pressure to 100 ml., and the mixed glycosides precipitated by the addition of ether. Concentration of the alcohol-ether solution gave a further quantity of mixed glycosides. The total yield varied between 1 to 2 grams.

(ii) Fresh green berries (112 g.) were rapidly minced, added to boiling ethanol (250 ml.), filtered and re-extracted five times with the same solvent. The combined alcoholic extracts were concentrated under reduced pressure to 200 ml. after which further distillation became impracticable owing to excessive foaming. The concentrate was extracted with ether to remove excess fats, when most of the mixed glycosides separated between the aqueous and ether layers. The ether was separated and the aqueous layer filtered. The solid was washed with ether when the mixed glycosides were obtained as a white amorphous solid slightly soluble in ethanol.

The aqueous filtrate was free from glycoside and on further evaporation gave a red syrup containing a large number of minute rhombohedra. Lixiviation with 95 per cent ethanol dissolved the syrup leaving a colourless crystalline solid; this was dissolved in water and reprecipitated by ethanol to give colourless rhombohedra, m. p. 134°.

(iii) The extraction of the different parts of the plant was carried out by either of the above two methods. To confirm the presence of small traces it was found expedient to hydrolyse the crude extract and weigh the aglycone. The yields of mixed aglycones were:— dried leaves 0·06 per cent, fresh leaves 0·02 per cent, flowers 0·01 per cent, black berries, seeds from black berries and bark, traces only.

Acid hydrolysis of the mixed glycosides

The mixed glycosides (400 mg.) were refluxed with a mixture of alcohol (20 ml.) and concentrated hydrochloric acid (5 ml.) when crystals began to separate after one hour. After three hours the solution was cooled and the product recrystallized from methanol to give a mixture of aglycones as long needles, m. p. 284°, unchanged by repeated crystallization.

Enzyme hydrolysis of the mixed glycosides

(i) *Isolation of cestrinase.* The dried berries (29 g.), completely defatted with ether, were covered with distilled water containing thymol and allowed to stand for 8 hours

at room temperature and 16 hours at 0°. The pulp was squeezed out and the cloudy liquid added to 95 per cent ethanol. The flocculent precipitate was collected in a centrifuge, redissolved in water (100 ml.) and the supernatant liquid again added to ethanol (5 volumes). The precipitate was suspended successively in 80 per cent, 95 per cent, and finally absolute alcohol. The solid was washed with dry acetone and dried in a vacuum desiccator leaving a light pink-brown fluffy powder.

(ii) The mixed glycosides (300 mg.), cestrinase (150 mg.) and distilled water (50 ml.) were allowed to stand at pH 5·6 at 37°. After nine days the mixture was treated with alcohol (5 volumes), filtered from precipitated enzyme and concentrated under diminished pressure. The turbid chloroform extract of the concentrate deposited on standing, a small quantity of unhydrolysed mixed glycoside and gave on evaporation, a small quantity of an amorphous solid, m. p. 273°, which yielded crystals from ethanol with the same melting point and showing no depression on admixture with gitogenin obtained via the acetate (see below).

Separation of the mixed aglycones

The mixed aglycones (5 g.) were boiled with excess acetic anhydride for 30 minutes, the reagent distilled off under diminished pressure and all traces finally removed by the addition of dry benzene which was distilled off. The residue was crystallized twice from ethanol to give gitogenin diacetate, m. p. 241 – 242°.

Found: C, 71·9; H, 9·7.

$C_{31}H_{48}O_6$ requires: C, 72·1; H, 9·4%.

This acetate (1 g.) was refluxed for 30 minutes with 10 per cent alcoholic potassium hydroxide (50 ml.), poured into water (100 ml.) and the solution extracted with ether. The solid from the ether extract was crystallized from ethanol to give long, colourless needles of gitogenin, m. p. 272 – 273°.

Found: C, 73·1; H, 10·3.

$C_{27}H_{44}O_4.C_2H_6O$ requires: C, 72·8; H, 10·5%.

After sublimation in high vacuum,

Found: C, 74·8; H, 10·1.

$C_{27}H_{44}O_4$ requires: C, 75·0; H, 10·3%.

The mother liquor from the crystallization of gitogenin diacetate on concentration gave digitogenin triacetate as long needles, m. p. 190° which was not raised further by recrystallization.

Found: C, 68·1, 68·6; H, 8·7, 8·9.

$C_{33}H_{50}O_8$ requires: C, 69·0; H, 8·8%.

Hydrolysis of this acetate by the method described above and crystallization from ethanol gave digitogenin as long, colourless needles, m. p. 284 – 285°.

After sublimation in high vacuum,

Found: C, 72·3; H, 9·7.

$C_{27}H_{44}O_5$ requires: C, 72·3; H, 9·9%.

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REFERENCES

[1] Thorburn, J. A., *Onderstepoort J. Vet. Sci. and Animal Husb.*, 1934, **2**, No. 2, 667.
[2] Marker, R. E., and Lopez, J., *J. Amer. Chem. Soc.*, 1947, **69**, 2383.
[3] *ibid.*, p. 2389.
[4] *ibid.*, p. 2387.
[5] Marker, R. E., *et alia*, *J. Amer. Chem. Soc.*, 1939, **61**, 2724.
[6] Jacobs, W. A., and Hoffmann, A., *J. Biol. Chem.*, 1926, **60**, 157.

CONDENSATION PRODUCTS OF CHLORAL WITH CERTAIN *p*-SUBSTITUTED PHENOLS AND SOME DERIVATIVES OF POSSIBLE CHEMOTHERAPEUTIC INTEREST

by

O. G. BACKEBERG

OPSOMMING

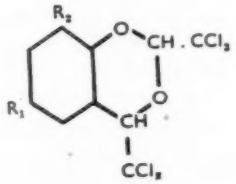
Die reaksie tussen chloraal en *p*-nitrofenol, soos deur Chattaway ontdek, wat tot die vorming van 6-nitro-2 : 4-bistrichlorometiel-1 : 3-bensdioksien (**I**, $R_1 = NO_2$; $R_2 = H$) lei, en wat later uitgebrei is na 'n aantal ander *p*-gesubstitueerde fenole, is verder ondersoek; as gevolg van die teenwoordigheid van die $-CCl_3$ groep in hierdie bensdioksien afleidinge, is sommige van hulle van chemoterapeutiese belang. Die resultate van toetse op vier van hierdie verbindinge word beskryf.

SUMMARY

The reaction between chloral and *p*-nitrophenol, discovered by Chattaway, leading to the formation of 6-nitro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (**I**, $R_1 = NO_2$; $R_2 = H$) and subsequently extended to a number of other *p*-substituted phenols, has been further investigated; owing to the presence of the group $-CCl_3$ in these benzdioxin derivatives, some of them are of chemotherapeutic interest. The results of tests on four of these compounds are reported.

During recent years[1–5] several investigators have studied the preparation of 1 : 1 : 1-trichloro-di-[*p*-aminophenyl]-ethane and some of them reported that it possesses pronounced anti-tubercular properties; furthermore, Lorenz[6] noted that it has been claimed that the corresponding di-[*p*-nitrophenyl]-compound is active against *Rickettsia mooseri* infection in mice. In view of the fact that chloral undergoes condensation with certain *p*-substituted phenols[7] to form compounds which, although not related to the above "DDT" type, nevertheless contain the lipoid-soluble group $-CCl_3$ and as such might form derivatives of possible chemotherapeutic interest, it was decided to undertake the preparation of a number of such compounds.

In 1926 Chattaway[7] reported that in the presence of concentrated sulphuric acid, chloral condenses with *p*-nitrophenol to form a stable, well-defined, crystalline compound in good yield, which proved to be 6-nitro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (**I**, $R_1 = NO_2$; $R_2 = H$).



In a series of subsequent publications Chattaway and his pupils[8–15] applied this reaction to a number of other *p*-substituted phenols and obtained the corresponding benzdioxin derivatives in good yield; however, they reported[10] that "5-nitrosalicylic acid, *p*-nitro-*o*-cresol and 2 : 4-dinitrophenol, in all of which one position ortho to the hydroxyl group is occupied, do not condense with chloral in presence of concentrated sulphuric acid. This may be due to the steric hindrance of the substituents ortho to the phenolic group preventing the addition which probably precedes the entrance of the $-CH(OH).CCl_3$ group into the nucleus."

A reinvestigation of this reaction has shown that not all *p*-substituted phenols form benzdioxin derivatives with chloral; thus, the mono-substituted phenols *p*-cresol, *p*-chlorophenol, hydroquinone, hydroquinone mono-benzyl ether and *p*-hydroxydiphenylamine formed only gummy products from which crystalline materials could not be isolated; so also for the di-substituted phenols 2-bromo-4-methyl-phenol, 2-methyl-4-bromophenol and 2 : 4- and 3 : 4-dimethylphenol; on the other hand, 2-chloro-4-nitrophenol and *p*-nitrosophenol did not appear to react at all. The following compounds, however, all of which contain a substituent ortho to the hydroxyl group, formed the corresponding benzdioxin derivatives:— 2 : 4-dichlorophenol, 2-nitro-4-methylphenol, 2-methyl-4-nitrophenol (which, according to Chattaway, did not react) and 2-nitro-4-chlorophenol. Consequently, the explanation for the fact that the compounds mentioned by Chattaway did not react must be sought in some cause other than steric hindrance.

Although *p*-chlorophenol did not form a benzdioxin derivative, it was nevertheless of interest to prepare 6-chloro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (**II**, $R_1 = Cl$; $R_2 = H$) from the corresponding 6-amino-compound (**IV**) by means of the Sandmeyer reaction, in order to investigate its insecticidal properties; it was found that both this compound as well as the 6 : 8-dichloro-compound (**III**, $R_1 = R_2 = Cl$) possessed no significant activity when tested on the common house-fly.

In view of what has been said above, it appeared worth while to test the four compounds in which $R_2 = H$ and $R_1 = NO_2$ (**I**), or NH_2 (**IV**), or SO_2NH_2 (**V**), or $NHSO_2C_6H_4NH_2(p)$ (**VI**); of these, the first three were prepared by Chattaway. The tests were carried out in the Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, U.S.A., by arrangement with Dr. E. Rhormann, Director of the Division of Organic Chemistry in that company, to whom the author expresses his grateful thanks. The results of these tests may be summarized as follows:—

All four compounds were ineffective in mice against influenza virus, MM poliomyelitis virus, *Streptococcus hæmolyticus*, tetanus toxin and typhoid. Compounds (**I**), (**IV**) and (**VI**) showed very low activity against *Entamœba histolytica*, *in vitro*; compound (**V**) was approximately one-fourth as active as carbasone oxide against *Entamœba histolytica*. Compound (**IV**) was tested *in vitro* against a human strain of tuberculosis and found to be inactive.

EXPERIMENTAL

Chattaway's procedure for the preparation of the benzdioxin derivatives was modified as follows:—

The phenol (10 g., 1 mol) was stirred mechanically with concentrated sulphuric acid (100 c.c.) and chloral hydrate (2·2 mols) added in portions during 30 minutes. Stirring was continued for a further hour and the reaction mixture (usually a clear solution) allowed to stand for 4 – 5 days. The dioxin derivative which had separated as a solid crust, was filtered from the acid through a glass "fritter" funnel, drained well and washed with water; the product was obtained pure by crystallization from glacial acetic acid and then from alcohol. The yields reported are weights of pure product obtained from 10 g. phenol.

In those cases in which the product was not a benzdioxin derivative, but the intractable gummy substance previously referred to, this substance began to separate almost immediately with the addition of the phenol, and was thus easily distinguishable from the reaction in which a benzdioxin was formed.

6 : 8-Dichloro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (III)

Long, colourless needles, m. p. 123°; yield, 6 g.

Found: Cl, 64·2.

$C_{10}H_4O_2Cl_8$ requires Cl, 64·5%.

After this work had been completed, an abstract[16] of a publication describing the preparation of this compound (m. p. 122 – 123°) became available.

6-Methyl-8-nitro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin

This compound was previously prepared by Irving and Curtis[15] who reported m. p. 175 – 176°. Prepared as above, it had m. p. 182°; yield, 10·8 g.

Found: N, 3·3.

$C_{11}H_7O_4NCl_6$ requires N, 3·3%.

6-Nitro-8-methyl-2 : 4-bistrichloromethyl-1 : 3-benzdioxin

Stout, colourless prisms, m. p. 152°; yield, 9 g.

Found: N, 3·5.

$C_{11}H_7O_4NCl_6$ requires N, 3·3%.

6-Amino-8-methyl-2 : 4-bistrichloromethyl-1 : 3-benzdioxin

The above nitro-compound was reduced as follows:— The nitro-compound (11·5 g.) was dissolved in glacial acetic acid (200 c.c.) with warming, acetic anhydride (17 c.c.) added, followed by crystalline stannous chloride (19 g.). The mixture was saturated with dry hydrogen chloride and then warmed on the water-bath for an hour. After cooling, the hydrochloride of the amine which had separated, was filtered off and stirred well with excess dilute sodium hydroxide; it was filtered, washed and crystallized from dilute alcohol, when it was obtained as fine, colourless needles, m. p. 169°.

Found: N, 3·6.

$C_{11}H_9O_2NCl_6$ requires N, 3·5%.

The benzoyl derivative, prepared by benzoylation in pyridine solution, crystallized from dilute acetic acid in colourless, microcrystalline needles, m. p. 201·5°.

Found: N, 3·0.

$C_{18}H_{13}O_3NCl_6$ requires N, 2·8%.

6-Chloro-8-nitro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin

Cream-coloured silky needles, m. p. 155°; yield, 5 g.

Found: N, 3·1.

$C_{10}H_4O_4NCl_7$ requires N, 3·1%.

6-Chloro-8-amino-2 : 4-bistrichloromethyl-1 : 3-benzdioxin

The nitro-compound (4 g.) was reduced by the method described above except that the hydrochloride of the amine did not separate. After the solution, saturated with hydrogen chloride, had been heated, it was filtered from a small quantity of insoluble material and poured into water. The amine separated as a gummy mass which solidified after standing overnight; it crystallized from dilute alcohol in colourless, microcrystalline needles, m. p. 114°; yield, 3·4 g.

Found: N, 3·5.

$C_{10}H_6O_2NCl_7$ requires N, 3·3%.

The amine was acetylated by boiling with acetic anhydride, and the solution poured into water; the product crystallized from dilute acetic acid in colourless, shining plates, m. p. 209°.

Found: N, 3·1.

$C_{12}H_8O_3NCl_7$ requires N, 3·0%.

6-Acetylsulphanilamido-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (VII)

($R_1 = NHSO_2C_6H_4NHCOCH_3(p)$; $R_2 = H$).

The amine (**IV**, $R_1 = NH_2$; $R_2 = H$; 12·2 g.) was dissolved in acetone (100 c.c.) and *p*-acetaminobenzenesulphonyl chloride (9·3 g.) and pyridine (8 c.c.) added. After standing overnight, the solution was heated to boiling, water added to incipient turbidity and cooled in the ice-chest for 12 hours. The solid which had separated, was filtered, washed with hot water and crystallized from dilute acetic acid; small, colourless needles, m. p. 238°; yield, 19 g.

Found: N, 4·8, 4·95.

$C_{18}H_{14}O_5N_2Cl_6S$ requires N, 4·8%.

6-Sulphanilamido-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (VI)

($R_1 = NHSO_2C_6H_4NH_2(p)$; $R_2 = H$).

The above crude acetylsulphanilamido-compound (15 g.) was dissolved in alcohol (150 c.c.) containing concentrated hydrochloric acid (25 c.c.) and water (50 c.c.). The solution was refluxed for 3 hours and then allowed to evaporate. The product crystallized from dilute acetic acid in colourless, shining plates, m. p. 201°; yield, 12 g.

Found: N, 5·1, 5·2; Cl, 39·5.

$C_{16}H_{12}O_4N_2Cl_6S$ requires N, 5·2; Cl, 39·4%.

6-Chloro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (II)

($R_1 = Cl$; $R_2 = H$).

Cuprous chloride was prepared by dissolving copper sulphate (40 g.) and sodium chloride (13·6 g.) in water (150 c.c.) and adding sodium metabisulphite (18·3 g.).

The cuprous chloride was filtered off and dissolved in a mixture of concentrated hydrochloric acid (30 c.c.) and water (30 c.c.). The amine (**IV**, 10 g.) was diazotized[8] and added in portions to the solution of cuprous chloride heated on the water-bath, heating being continued for a further hour. The brown product which had separated was filtered off, washed and crystallized thrice from dilute alcohol (charcoal); colourless, shining prisms, m. p. 123°; yield, 5·1 g.

Found: Cl, 60·8.

$C_{10}H_3O_2Cl_7$ requires Cl, 61·3%.

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REFERENCES

[1] Burger, A., Graef, E., and Bailey, M. S., *J. Amer. Chem. Soc.*, 1946, **68**, 1725.
[2] Kirkwood, S., Phillips, P. H., and McCoy, E., *ibid.*, 1946, **68**, 2405.
[3] Kirkwood, S., and Phillips, P. H., *ibid.*, 1947, **69**, 934.
[4] Balaban, I. E., and Levy, M. B., *J. Chem. Soc.*, 1948, 1458.
[5] Weizmann, M., Israelashvili, S., and Papo, R., *J. Amer. Chem. Soc.*, 1948, **70**, 4263.
[6] Lorenz, W., *Chem. Ber.*, 1948, **81**, 422 (footnote).
[7] Chattaway, F. D., *J. Chem. Soc.*, 1926, 2720.
[8] Chattaway, F. D., and Calvet, F., *ibid.*, 1927, 685.
[9] Chattaway, F. D., and Morris, A. A., *ibid.*, 1927, 2018.
[10] Chattaway, F. D., and Calvet, F., *ibid.*, 1928, 1088;
[11] *Ibid.*, p. 2913.
[12] Chattaway, F. D., and Irving, H., *ibid.*, 1931, 2492.
[13] Chattaway, F. D., and Bell, A. E., *ibid.*, 1934, 43.
[14] Chattaway, F. D., and Irving, H., *ibid.*, 1934, 325.
[15] Irving, H., and Curtis, E. G., *ibid.*, 1943, 319.
[16] Ettel, V., and Weichet, J., *Chem. Abstr.*, 1949, **43**, 1754.

THE SPECTROCHEMICAL DETERMINATION OF MAGNESIUM IN CAST IRON

by

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SUMMARY

Two methods for the determination of magnesium in ductile cast iron are described. These methods are:—

(i) A "wet" spark method having an accuracy of better than 4 per cent.
(ii) A D.C. arc method having an accuracy of 7 per cent.

The attachment for the direct sparking of solutions is described.

OPSOMMING

Die volgende twee metodes vir die bepaling van magnesium in gietyster word beskryf:—

(i) 'n „Natvonk"-metode met meer akkuraatheid as 4 persent.
(ii) 'n Gelykstroom-lugboogmetode met 'n akkuraatheid van 7 persent.

'n Apparaat vir direkte vonking in oplossings word beskryf.

INTRODUCTION

The inclusion of trace amounts of magnesium in cast iron has a marked influence on its properties, especially as regards the ductility of the metal. The magnesium concentrations which promote the formation of nodular graphite structures in cast iron are of the order of 0·01 per cent to 0·1 per cent magnesium. The chemical determination of magnesium at these concentrations takes about five hours[1]. This chemical analytic method is therefore too slow and cumbersome for production control.

Due to the interest of a South African firm in a possible spectrographic method for production control of ductile cast iron, it was decided to survey possible spectrographic techniques.

Nahstoll and Veldhuis[2] have published a procedure in which the magnesium content of a number of cast iron rods were primarily determined by means of a solution technique. These rods were then subsequently used as the spectrographic standards. In their solution technique 0·03 ml. aliquots, from synthetically prepared standard solutions and from the solutions of the rods, were dried on the ends of graphite electrodes. The spectra were excited in a high-voltage spark source of the auxiliary air-gap type. An accuracy of 10 per cent is reported, using the line pair Mg 2802·7/Fe 2788·1. In their method, using the solid electrodes, the spectra were excited by means of a high-voltage spark source of the mechanical interrupter type. The analysis line pairs used were Mg 2795·53/Fe 2823·27 for 0·005 per cent to 0·025 per cent magnesium and Mg 2852·13/Fe 2823·27 for 0·02 per cent to 0·15 per cent magnesium. An accuracy of about 10 per cent is reported also for this method.

Rozsa[1], also using a solution technique but drying the aliquots on pure aluminium electrodes, reported an accuracy of 5 per cent. The analysis line pair used by Rozsa was Mg 2802·7/Fe 2598·4.

In view of the success of these two spectrographic techniques and because of the unavailability of spectrographic standards, it was decided to try and develop spectrographic solution techniques to solve this problem. Two techniques have been successfully developed, *viz.*, a "wet" spark method and a D.C. arc method.

The principal advantages of a solution technique are:—

(i) Suitable standards can be readily synthesized.
(ii) The effects of the metallurgical history of the sample on the intensity ratio of the analysis line pair are avoided.
(iii) Better sampling is possible because a relatively large sample can be brought into solution from which aliquots for analysis are taken.

The principal disadvantages of solution techniques are:—

(i) The methods are usually slow.

(ii) No information on the micro-structure of the original sample is obtainable. Erratic analytical results, using solid electrodes, are often an indication of a sample with a non-uniform structure.

Preparation of solutions

(a) *Standards*

Pure magnesium-free iron was dissolved in distilled nitric acid and the solution made up to contain 10 per cent iron. Using this iron solution and suitable magnesium nitrate solutions, a series of standard solutions with concentration ratios corresponding to 0·0125, 0·025, 0·05, 0·1, 0·2 and 0·4 per cent magnesium in iron was made up. These solutions contained about 10 per cent nitric acid and had an iron content of 5 per cent. Although the acid content of the solutions has no effect on the intensity ratios, it was found advisable to make solutions containing about 10 per cent acid because at this acid concentration the spark discharge was found to be the most stabilized.

(b) *Samples*

Samples, in the form of drillings or cuttings, were weighed and dissolved in pure nitric acid. These solutions were then made up to a metal content of 5 per cent.

The spark method

The slowness of solution techniques is principally due to the time required for the preparation of the electrodes when the sample solutions have to be dried on the electrode ends. One method to overcome this disadvantage is the use of a solution excitation attachment[3]. An attachment for the direct excitation of solutions which fits the arc stand described by Strasheim[4] was designed. The design of this attachment is shown in Fig. 1.

It consists of a brass bracket (1) through which two holes are drilled to accommodate the stainless steel spindle (2). The spindle has a tapered end on to which the rotating electrode (3) fits and is kept in position by two brass stop-collars (4) and (5). The bracket is cut to form a rectangular stem which fits snugly into one of the lower electrode clamp holes of the arc stand. A hole is drilled in the stem to accommodate a carbon brush (6). This brush is incorporated to minimize the sparking from the bracket to the spindle. The other end of the spindle is connected to the shaft of a small electric motor of which the speed of rotation can be varied. A piece of rubber pressure tubing connects the spindle with the shaft of the motor. This tubing serves the triple purpose of driving the spindle, insulating the motor from the high-voltage spark and allowing small adjustments of the position of the rotating electrode without a corresponding adjustment in the position of the motor. The rotating electrodes are graphite discs of 16 mm. diameter and a 6 mm. width with a centre hole tapered to fit the tapered end of the spindle firmly. Submerged to a depth of about 2 mm., the electrodes rotate in a glass boat placed on the platform formed by the lower electrode holder.

Using an A.R.L. spark generator the optimum conditions for the determination of magnesium in cast iron were established. These conditions are listed in Table I.

TABLE I

Experimental conditions for the determination of magnesium in cast iron using the "wet" spark method.

Spectrograph	Hilger medium, quartz.
Slit width	0·02 mm.
Plate	Ilford thin film half tone.
Primary voltage on spark generator	70 volts.
Energy	2/3 kVA.
Secondary inductance	0·09 millihenry.
Electrode separation	2·5 mm.
Lower electrode	A graphite disc of 16 mm. diameter, 6 mm. width rotating at 9 revolutions per minute.
Upper electrode	A graphite rod of 6 mm. diameter with a hemispherical end.
Pre-spark period	60 seconds.
Exposure	Three consecutive exposures of 10 seconds each.
Line pairs	Mg 2802·7/Fe 2804·5 for 0·01 per cent – 0·1 per cent magnesium. Mg 2790·8/Fe 2788·1 for 0·01 per cent – 0·4 per cent magnesium.

The only excitation parameters which must be critically controlled are the secondary inductance and the electrode separation. An increase in the inductance of the discharge circuit decreases the intensity ratio of the analysis and internal standard lines. This decrease is accompanied by a decrease in the reproducibility of the intensity of the analysis line pair ratio. Another effect of increasing secondary inductance is a decrease in the background density of the spectrum. This is probably due to the suppressing of bands.

The control of the electrode separation is critical because it has a marked influence on the intensity ratios of the analysis line pairs. Intensity ratios were determined for the same sample for electrode separations varying from 1 mm. to 4 mm. and it was found that the ratio decreases with increasing electrode separation to a minimum and then increases sharply. This minimum in the ratio corresponds to an electrode separation of 2·5 mm. Because of this effect it is necessary to adjust the electrode

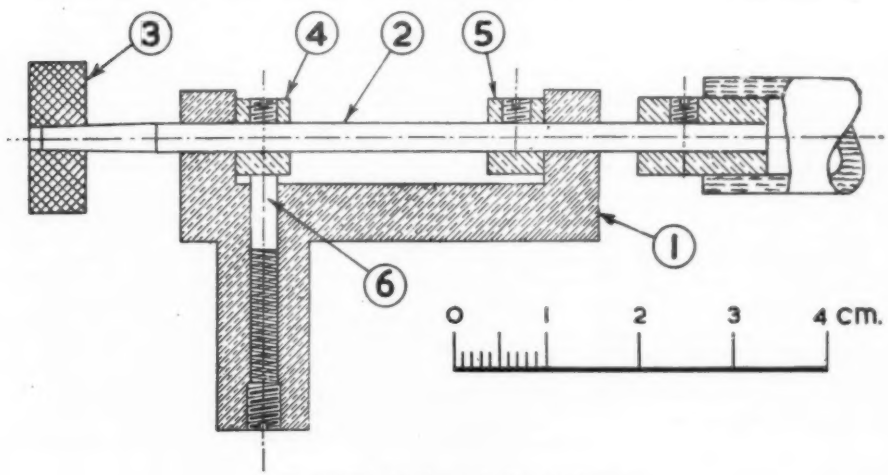

FIG. 1.—The solution excitation attachment.

separation to within 0·1 mm. This accuracy in setting is readily obtained with the described assembly and carefully cut rotating electrodes.

Special care is necessary to avoid contamination of either the electrodes or solutions, especially for magnesium concentrations below 0·1 per cent. Commercial electrodes were found to be contaminated to such a degree that purification was necessary. Purification was carried out according to the method described by Strasheim[5].

The long pre-spark period of 60 seconds is necessary to obtain spectrograms of constant density. Sparking-off effects are present only for about 15 seconds of sparking and are totally absent for a pre-spark period of 60 seconds.

Photometry

The transmission values of the analysis and internal control lines were measured with the aid of a Leeds and Northrup microphotometer. The plates were calibrated by means of the stepped sector method described by Churchill[6], Schmidt, Manders and Van Wyk[7] and Strasheim[8]. Instead of using the density as the one variable the transformed density or Seidel-function W was used. The Seidel-function[9] is given by the equation

$$W = \log (A_o/A-1),$$

where A_o = clear plate deflection of microphotometer
and A = deflection of the microphotometer through the line.

The use of the Seidel-function has the advantage of making both the preliminary curve and the calibration curve approximate straight lines. The intensity ratios were calculated from the transmission data on a calculating board fitted also with Seidel-scales. No background corrections were made.

The use of the calculating board and the deletion of background corrections shorten the time required for analysis considerably.

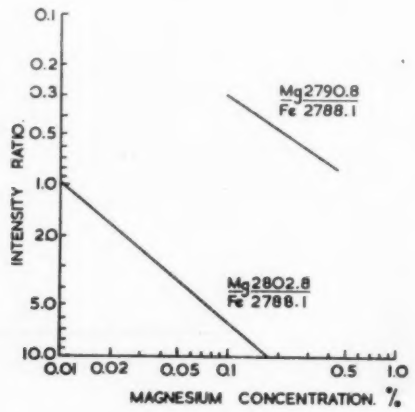

FIG. 2
Analysis curves for magnesium in cast iron using the "wet" spark method.

A skilled operator and one assistant can analyse from 40 to 50 samples in triplicate per day of seven hours. The time required per sample increases, however, sharply when the number of samples becomes small. A single sample requires about one hour for an analysis in triplicate.

Analysis curves and accuracy

The analysis curves for the concentration range from 0·01 per cent magnesium to 0·4 per cent magnesium are shown in Fig. 2.

The accuracy of the method is 4 per cent standard deviation for Mg 2790·8/Fe 2788·1 and 5 per cent for the line pair Mg 2802·7/Fe 2804·5 for a single determination per sample. The accuracy can be improved to about 3 per cent standard deviation by making the analysis in triplicate.

The D.C. arc method

In this method the solutions are prepared in the same way as for the spark method. Aliquots of 0·1 ml. are dried in the cups of purified graphite electrodes. This is accomplished by heating the electrodes to about 300°C. and introducing the solution very slowly into the cup by means of a micro-pipette. On contact with the electrode the solution evaporates and leaves the cup impregnated with the salts of the solution. It is necessary to introduce the solution in two steps of 0·05 ml. each and heating the electrode between the two impregnations.

The electrodes are arced and the spectra photographed under the conditions listed in Table II.

TABLE II

Conditions for the determination of magnesium in cast iron using D.C. excitation.

Spectrograph	..	Hilger Littrow, with quartz optics.
Slit width	.. ..	0·015 mm.
Plate	.. ..	Ilford thin film half tone.
Light source	..	A D.C. arc of 13 amps at 230 volts.
Lower electrode	..	A 6 mm. graphite electrode cut to form a cup of 6 mm. depth, 3 mm. diameter and a wall-thickness of 0·5 mm.
Upper electrode	..	A 6 mm. graphite electrode with a rounded end.
Electrode separation		9 mm. Centre 4 mm. portion of arc photographed.
Exposure time	. ..	Sample burnt to completion—about 80 seconds.

The use of the high dispersion spectrograph is necessary to isolate the analysis lines of magnesium from the iron lines emitted in an arc.

For concentrations between 0·01 per cent and 0·1 per cent the line pair Mg 2802·7/Fe 2779·3 is measured and for concentrations above 0·1 per cent the line pair Mg 2779·8/Fe 2779·3. The photometry of these lines is carried out in the same way as for the spark method. No background corrections are made because the background intensity is kept low by cutting off all light emitted from the glowing electrodes. The analysis curves for the line pairs are given in Fig. 3. The curve for the line pair Mg 2779·8/Fe 2779·3 starts bending towards the concentration axis for concentration values below 0·08 per cent. This is due to the fact that at these concentrations the line intensities start to approach the background intensities.

The average accuracy for both line pairs over the whole concentration range is 7 per cent standard deviation.

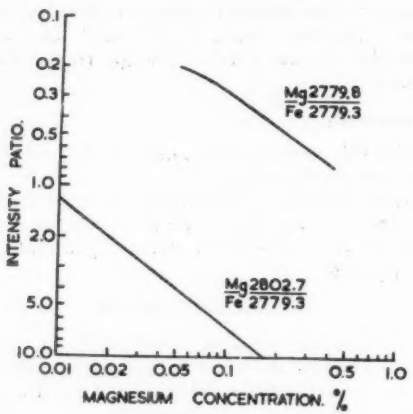

FIG. 3
Analysis curves for magnesium in cast iron using the D.C. arc method.

This method is considerably slower than the spark method. A maximum of 30 samples can be analysed per day by a skilled operator and an assistant as compared with fifty samples when the spark method is used. This slowness is principally due to the time required for the preparation of electrodes.

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REFERENCES

[1] Rozsa, J. T., *The Iron Age*, 1949, **164**, No. 25, 73.
[2] Bryan, Ford R., Nahstoll, G. A., and Veldhuis, H. D., *A.S.T.M. Bulletin*, 1949, No. 162, 69.
[3] Applied Research Laboratories, Spectrographers' News Letter **3**, No. 2.
[4] Strasheim, A., *Spectrochimica Acta*, 1950, **4**, 2.
[5] Strasheim, A., Union of South Africa, Department of Agriculture Science Bulletin No. 264.
[6] Churchill, J. R., *Ind. Eng. Chem.* (Anal. Ed.), 1944, **16**, 653.
[7] Schmidt, R., Manders, H., and Van Wyk, G. ., *Rec. trav. chim.*, 1948, **67**, 745.
[8] Strasheim, A., in press.
[9] Kaiser, H., *Spectrochimica Acta*, 1941–44, **2**, 1.

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